

Calcium, Phosphorus, and Other Minerals

Scope

This method is only applicable to non mineral-mix feeds.

Summary

A ground portion of the sample is dry ashed. The ash is dissolved with acid and diluted to a certain volume. The resultant solution is then analyzed by atomic absorption for mineral elements except phosphorus. Phosphorus is determined by a gravimetric procedure.

Comments

Dissolved ash solutions prepared by this procedure can be screened for minerals including sodium (from salt) and phosphorus by Inductively Coupled Plasma Atomic Emission Spectroscopy. Run 10% spikes, controls, and duplicates for atomic absorption analysis, and 10% controls and duplicates for gravimetric phosphorus analysis.

Apparatus and Materials

- A. Well-glazed porcelain dishes.
- B. Watch glasses to fit porcelain dishes.
- C. Funnels.
- D. Whatman #43 filter paper.
- E. 100 ml volumetric flasks.
- F. 500 ml Erlenmeyer flasks.
- G. 50 ml Erlenmeyer flasks.
- H. Gooch crucibles.

- I. Glass fiber filter paper to fit gooch crucibles.
- J. Desiccator.
- K. Muffle furnace.
- L. Hot plate.
- M. Atomic Absorption Spectrophotometer.
- N. Inductively Coupled Plasma Emission Spectrometer.
- O. Oven.

Reagents

- A. 3N HCl: add 258 ml of concentrated HCl to about 500 ml of deionized water in a 1 liter volumetric flask. Allow to cool and dilute to volume with deionized water and mix.
- B. 0.5N HCl: add 40 ml concentrated HCl to 920 ml of deionized water and mix.
- C. Lanthanum stock solution: 50 g La/L. Add 250 ml concentrated HCl to 58.65 g La_2O_3 in a 1 L volumetric flask. Add acid slowly as the reaction is violent and produces heat. Cool, dilute to volume with deionized water and mix.
- D. Quimociac reagent: Dissolve 70 g sodium molybdate $\cdot 2\text{H}_2\text{O}$ in 150 ml deionized H_2O . Dissolve 60 g citric acid in mixture of 85 ml HNO_3 and 150 ml deionized H_2O , and cool. Gradually add the molybdate solution to citric acid - HNO_3 mixture with stirring. Dissolve 5 ml synthetic quinoline in a mixture of 35 ml HNO_3 and 100 ml deionized H_2O . Gradually add this solution to the molybdate - citric acid - HNO_3 solution, mix, and let stand 24 hr. Filter, add 280 ml acetone, dilute to 1 liter with deionized H_2O and mix.
- E. Commercial atomic absorption standards for elements to be analyzed.
- F. 1 + 1 nitric acid: combine equal portions of nitric acid and deionized water. Always add the acid to the water.

Procedure

A. Sample preparation: (Atomic absorption analysis)

1. Weigh 2-10 g of ground sample to the nearest 0.0001 g into a well-glazed porcelain dish. Record the sample weight.
2. Place the dish in a cold muffle and heat to 550°.
3. Maintain at 550° for 4 hours and then cool.
4. Cover the dish with watch glass and carefully add 10 ml of 3N HCl.
5. Boil gently on a hot plate for 10 minutes, remove and allow to cool.
6. Filter through Whatman #43 paper into a 100 ml volumetric flask.
7. Rinse the watch glass and dish into the funnel and rinse the funnel after filtration is complete. Use deionized water for rinsing.
8. Dilute to volume with deionized water and mix.

B. Sample preparation: (ICP screen)

Weigh 2-10 g of ground sample to the nearest 0.0001 g into a 250 ml Volume metric flask. Record the sample weight.

1. Place the flask in a cold muffle and heat to 550°.
2. Maintain at 550° for 15-18 hours and then cool.
3. Add 10 ml of 3N HCl.
4. Boil gently on a hot plate for 10 minutes, remove and allow to cool.
5. Dilute to volume with deionized water and mix.

C. Atomic absorption analysis for calcium and other minerals:

1. Prepare appropriate dilutions of the sample solutions to bring the expected mineral concentration into the range of the standard curve. Use 0.5N HCl

as the diluent.

2. The sample solutions for calcium analysis must contain 1% lanthanum if an air/acetylene flame is used. This can be accomplished by pipeting 20 ml of the final dilution into a 25 ml volumetric flask and diluting to volume with the lanthanum stock solution.
3. Consult the operator's manual for the instrument to be used to perform the instrumental analysis.
4. Read and record the absorbance values for each standard.
5. For instruments having concentration mode, calibrate in this mode using the appropriate calibration standards.
6. Read the concentration of the element of interest in each sample or have it printed out where this capability is available.
7. Run 10% spikes and duplicates.
8. Recheck the calibration standards after every 10 samples are analyzed and recalibrate if necessary.

D. Gravimetric analysis of phosphorus:

1. Pipet an aliquot of the prepared sample solution (A.8.) containing ≤ 10.9 mg of phosphorus into a 500 ml erlenmeyer.
2. Dilute to about 50 ml with deionized water, add 10 ml of 1 + 1 nitric acid and boil for 10 minutes on a hot plate in a hood.
3. Cool, dilute to about 150 ml with deionized water and add 50 ml of quimociac reagent from a 50 ml erlenmeyer flask.
4. Invert the 50 ml erlenmeyer in the opening of the 500 ml Erlenmeyer, place on the hot plate and boil for one minute.
5. Cool to room temperature and swirl 3-4 times during cooling.
6. Filter into a gooch crucible containing glass fiber filter paper. The gooch with paper should be dried at 250° for 1/2 hour, cooled in a desiccator and

weighed to the nearest 0.0001 g before filtering.

7. Wash the precipitate with five 25 ml portions of deionized water.
8. Dry the crucible and contents 1/2 hr. at 250°, cool in a desiccator, and weigh to the nearest 0.0001 g.

E. Screening for Minerals by ICP:

1. Dilute any prepared sample solution (A.8.), if necessary, with 0.5N HCl to bring element concentration into ICP standard curve range.
2. Pour sample and standard solutions into ICP autosampler tubes.
3. Set up 10% spikes and duplicates.
4. Work with an experienced ICP operator to set up the instrument and analyze the samples.
5. Record the emission counts for each standard.
6. To have the ICP computer calculate results in %, divide the standard concentration (ppm) by 10,000 before entering into the standards table. Salt analysis is done on the basis of sodium, so the sodium concentration (ppm) needs to be multiplied by 2.542 after being divided by 10,000. The sample weight and solution volume need to be entered in the sample method file data section.

F. Calculations:

1. For atomic absorption results where element concentrations are determined as ug/ml, calculate the % of the element as follows:

$$\% \text{ element} = (\text{ug/ml in final diln})(F/\text{sample wt})(10^{-4})$$

$$F = \frac{(\text{ml original volume})(\text{each intermediate volume})(\text{final volume})}{(\text{each intermediate aliquot})(\text{final dilution aliquot})}$$

2. Calculate the % phosphorus from the gravimetric analysis as follows:
 - a. First calculate the weight of the precipitate as follows:

(wt of gooch + paper + ppt) - (wt of gooch + paper) = wt ppt

- b. Calculate % P as follows:

$$\% P = \frac{(\text{wt of ppt.})(0.01400)(\text{Original solution volume})(100)}{(\text{wt of sample})(\text{aliquot taken for precipitation})}$$

3. The ICP or AA operator can calculate the spike recoveries. Consult QC charts to determine if recoveries are acceptable. If recoveries are not acceptable, the spike should be redone to determine if the entire run needs to be repeated.
4. The ICP results will be automatically calculated if the computer was set up to do so. The ICP operator can perform data reduction and will be able to transfer satisfactory results from the ICP computer to the laboratory information management system.

Quality Control

- A. For minerals except phosphorus:

1. Check and document the temperature of the ashing furnace at least once every three months.
2. Monitor the length of time the samples are ashed. Should be four hours.
3. Use ≥ 2 ml pipets and ≥ 25 ml volumetric flasks for any dilutions.
4. Record the adsorbance value or emission counts for each standard from each run.
5. Keep a record of wavelengths and analytical ranges used for each element.
6. Run a spike for every 10 samples.
 - a. Enter spike recoveries into the computer QC system so that a standard deviation can be calculated.
 - b. Spike recovery should be within two standard deviations of the mean recovery. If it is not, rerun the spike and adjust conditions

until acceptable recovery is obtained and rerun the sample set if necessary.

B. For phosphorus:

1. Monitor time.
 - a. Boiling after the addition of 1 + 1 HNO₃ should be done for ten minutes.
 - b. After the addition of the quimociac reagent solution should be boiled for one minute.
 - c. Crucibles and precipitate should be dried for 30 minutes at 250°C.
2. Check the temperature of the drying oven before use with a calibrated thermometer and document on the worklist.

Bibliography

Official Methods of Analysis (1984) 14th Ed., AOAC, Washington, D.C., secs. 7.096-7.100, 2.041, 2.028(b)